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**(54) MANUFACTURE OF LITHOGRAPHIC PRINTING FORMS**

**HERSTELLUNG VON LITHOGRAPHISCHEN DRUCKFORMEN**

**FABRICATION DE FORMES D'IMPRESSION LITHOGRAPHIQUES**

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**EP-A- 0 823 327** **WO-A-97/39894**  
**GB-A- 1 245 924** **US-A- 4 532 005**

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**EP 1 024 958 B1**

**Description**

**[0001]** The present specification relates to methods of manufacturing lithographic printing form precursors. The invention relates further to such lithographic printing form precursors *per se*, and to their use.

**[0002]** The art of lithographic printing is based on the immiscibility of ink, generally an oily formulation, and water, wherein in the traditional method the ink is preferentially retained by the image or pattern area and the water or fountain solution is preferentially retained by the non-image or non-pattern area. When a suitably prepared surface is moistened with water and an ink is then applied, the background or non-image area retains the water whilst the image area accepts ink and repels the water. The ink on the image area is then transferred to the surface of a material upon which the image is to be reproduced, such as paper, cloth and the like. Commonly the ink is transferred to an intermediate material called the blanket which in turn transfers the ink to the surface of the material upon which the image is to be reproduced.

**[0003]** New types of "waterless" lithographic printing employ only an oily ink material and preferentially ink-accepting image areas and ink-repelling non-image areas on the printing form.

**[0004]** A generally used type of lithographic printing form precursor (by which we mean a coated printing form prior to exposure and development) has a radiation sensitive coating applied to an aluminium substrate. Negative working lithographic printing form precursors have a radiation sensitive coating which when imagewise exposed to radiation of a suitable wavelength hardens in the exposed areas. On development the non-exposed areas of the coated composition are removed leaving the image. On the other hand positive working lithographic printing form precursors have a radiation sensitive coating, which after imagewise exposure to radiation of a suitable wavelength becomes more soluble in the exposed areas than in the non-exposed areas, in a developer. In both cases only the image area on the printing form itself is ink-receptive.

**[0005]** The differentiation between image and non-image areas is made in the exposure process where a film is applied to the printing form precursor with a vacuum to ensure good contact. The printing form precursor is then exposed to a radiation source; conventionally this has been a UV radiation source. In the case where a positive form precursor is used, the area of the film that corresponds to the image in the printing form precursor is opaque so that no light will strike the printing form precursor, whereas the area on the film that corresponds to the non-image area is clear and permits the transmission of light to the coating which becomes more soluble and is removed on development.

**[0006]** Most positive working systems rely on the inhibition of the inherent solubility of phenolic resins, in suitable developers. Traditionally this has been achieved through the use of diazide moieties, especially naphthoquinone diazide (NQD) moieties, to provide compositions which only following exposure to UV radiation are soluble in the developer.

**[0007]** As demands on the performance of UV sensitive positive working coatings have increased so NQD technology has become limiting. In addition, digital and laser imaging technology is making new demands on coatings for lithographic printing.

**[0008]** It is known from GB 1245924 that the solubility of phenolic resins in lithographic developers may be increased by the application of heat. The heat may be delivered by infra-red radiation, assisted by radiation absorbing components such as carbon black or Milori Blue (C.I. Pigment Blue 27). However the developer resistance of the non-exposed areas to commercial developers is low, and the solubility differential is low compared to the commercial UV sensitive compositions containing NQD moieties.

**[0009]** We have devised new positive working heat sensitive systems comprising phenolic resins, to meet the new demands. Our new systems and methods are the subject of our patent applications WO 97/39894, WO 98/31544, WO 99/01795, WO 98/01796 and WO 99/21725, all unpublished at the priority date of this application. We have observed that in our new systems there may be an alteration in their sensitivity over time, after the heat sensitive composition has been applied to a substrate and dried, such effect being the result of reduced developer solubility of the unexposed compositions with time prior to exposure. Thus when we mention "sensitivity" in this specification we are considering this in the context of the entire process of exposure and development. We are not referring to the matter of how the areas of the composition which are exposed react to that exposure. Sometimes this "sensitivity" is called "operating speed" in the art.

**[0010]** We have devised a process which improves the new systems mentioned above, such that a consistent and stable material can be supplied to an end user. The invention may also be applied to other compositions containing phenolic resins, for example those of GB 1245924 mentioned above, as well as those of US 5491046, 5466557, 5372915, 5372907 and US 4708925, described hereinafter.

**[0011]** In accordance with a first aspect of the invention there is provided a method of manufacturing a printing form precursor which comprises a coating on a substrate, the coating comprising a positive working composition which comprises a phenolic resin, wherein the method of manufacturing comprises the application of the composition in a solvent to the substrate, the drying of the composition, and the subsequent heat treatment of the coated substrate wherein the heat treatment is carried out for at least 4 hours.

**[0012]** Preferably the composition of the precursor manufactured by the method of the invention is heat sensitive, such that its solubility in a developer increases in heated areas during patternwise exposure. Suitably it may be pat-

ternwise exposed by direct heat, or by charged particle radiation or electromagnetic radiation, in each case converted to heat by the coating. In the latter case the electromagnetic radiation to which the coating is sensitive is preferably of wavelength exceeding 450 nm (i.e. entirely or predominantly above 450 nm), preferably exceeding 500 nm, more preferably exceeding 600 nm. In patternwise exposing the precursor the use of electromagnetic radiation is preferred.

**[0013]** A said preferred, heat sensitive, composition preferably includes a modifying means for modifying the properties of the composition. Such a modifying means is preferably arranged to alter the developer solubility of the composition compared to when said modifying means is not present in a said composition. Said modifying means may be covalently bonded to said phenolic resin or may be a compound which is not covalently bonded to said phenolic resin.

**[0014]** Said modifying means may be selected from:

- functional groups Q, as described in WO 99/01795;
- diazide moieties;
- nitrogen containing compounds wherein at least one nitrogen atom is either quaternized, incorporated in a heterocyclic ring or quaternized and incorporated in a heterocyclic ring, as described in WO 97/39894;
- latent Bronsted acids, onium salts or acid generating compounds as described in any statement hereinafter with regard to further compositions.

**[0015]** Said heat sensitive composition preferably passes tests 1 to 5 described in WO 97/39894, wherein a reference in the tests to an "active polymer" should be substituted with a reference to said phenolic resin, described above in the absence of said modifying means; and a reference to a "reversible insolubiliser compound" should be substituted with a reference to said modifying means.

**[0016]** As indicated above the invention can be applied to compositions containing diazide moieties. We have discovered that compositions containing diazide moieties may be patternwise exposed other than by UV radiation, for example by direct heat or by charged particle radiation or by electromagnetic radiation exceeding 500 nm. This invention is described in WO 98/01796. Infra-red radiation is preferred for the exposure process for such compositions and such compositions preferably contain a suitable infra-red radiation absorber. The invention may be applied with benefit to any such compositions but may also be applied to compositions containing diazide moieties, and intended or adapted for traditional UV exposure methods.

**[0017]** However, the preferred embodiments of the present invention involve the heat treatment of compositions which do not contain diazide moieties.

**[0018]** The composition is preferably such that its solubility in a developer is not increased by incident UV radiation; thus also passing test 6 described in WO 97/39894.

**[0019]** It is found that by carrying out a suitable heat treatment the sensitivity of the composition may be rendered less variable, over time. Furthermore, we have found that some compositions can only be exposed in a practicable manner if they have been given a heat treatment in accordance with the present invention, during the manufacture of the respective precursors.

**[0020]** In general terms it may be stated that to achieve good results the heat treatment should employ an elevated temperature, for an extended period; but the range of effective conditions, and the optimal conditions to achieve a substantially constant sensitivity over time, and at a practicable level, will vary from case to case, and can readily be determined by trial and error. We believe that a suitable heat treatment accelerates the formation of a stable network structure within the composition. If the elevated temperature is too low we believe the time required for this stable network structure to form is too long to be practicable. Furthermore in relation to the minimum suitable temperature it should be borne in mind that the elevated temperature should desirably not be less than that which the precursor might typically be subjected to in transit or in storage, or otherwise changes in sensitivity may occur. Consequently we favour carrying out the heat treatment at a temperature of at least 40°C, preferably at least 45°C, most preferably at least 50°C. As regards the upper limit, we believe that at too high a temperature the time for which the heat treatment should be carried out in order to obtain a desired level and stability of sensitivity is likely to be overly critical, and that even when the sensitivity is adequately stable, it is likely to be too low to be of use. Again, trial and error can easily be used to make this determination but as a guide we favour using a temperature not in excess of 90°C, preferably not in excess of 85°C, most preferably not in excess of 60°C.

**[0021]** We believe that temperatures in the range 50-60°C (inclusive) may be most favoured in the method of the present invention.

**[0022]** The time for the heat treatment can also be determined by trial and error. Generally, the lower the temperature for the heat treatment, the longer the time should be. In all cases however the heat treatment is carried out for at least 4 hours, as defined in claim 1, though we favour carrying out the heat treatment for at least 24 hours and most preferably

for at least 48 hours, especially in the case of the lower temperatures.

[0023] The time and temperature conditions for the heat treatment may be contrasted with the time and temperature conditions for the drying step. The heat treatment step preferably employs a lower temperature and a longer time, than the drying step. In the drying step the aim is to "flash dry" the composition. The time may typically be 15-600 seconds, especially 25-250 seconds and the temperature may typically be at least 70°C, suitably 80-150°C, especially 90-140°C. The drying step should be carried out until the coating is self-supporting and dry to the touch. However it is not necessary (and may not even be possible) to remove all the solvent, in the drying step (or in the later heat treatment step). Indeed the residual solvent content may be regarded as an additional composition variable by means of which the composition may be optimised, as we have found that higher amounts of solvent may be beneficial in the later patternwise exposure and development process; compositions with higher amounts of retained solvent appear to be more sensitive than corresponding compositions with lower amounts of retained solvent.

[0024] The time and temperature conditions for the heat treatment of the invention, carried out by the manufacturing of the precursor, may also be contrasted with the delivery of heat during the later exposure processes, for those preferred compositions which are heat sensitive, the latter delivery of heat being of very short duration and very high intensity.

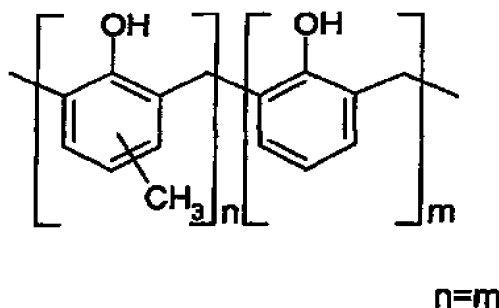
[0025] The solvent itself is not critical; any solvent in which the composition can be dissolved and which may be removed by evaporation after coating may be used.

[0026] It will be appreciated that a primary object of the invention is to render the sensitivity (as previously defined) of the composition less variable over time. This is suitably assessed over a period of time which is the longest interval likely, between the manufacture of the printing form precursor and the use of the printing form precursor, by a customer. We regard one year as being a suitable period of time, for this assessment. In absolute terms, preferably the heat treatment is such that the sensitivity reduction in a given practical developer, for example 14 wt% sodium metasilicate pentahydrate in water, of said composition over a one year period after the heat treatment does not exceed 15%; and preferably does not exceed 10%.

[0027] A further object of the present invention is that the sensitivity of the preferred compositions should be at a practicable level, after the heat treatment; but suitably no more than 400 mJcm<sup>-2</sup>, preferably no more than 250 mJcm<sup>-2</sup>, most preferably no more than 200 mJcm<sup>-2</sup>.

[0028] Novolak resins are useful in this invention, suitably being condensation reaction products between appropriate phenols, for example phenol itself, C-alkyl substituted phenols (including cresols, xylenols, p-tert-butyl-phenol, p-phenylphenol and nonyl phenols), diphenols e.g. bisphenol-A (2,2-bis(4-hydroxyphenyl)propane), and appropriate aldehydes, for example formaldehyde, chloral, acetaldehyde and furfuraldehyde. The type of catalyst and the molar ratio of the reactants used in the preparation of phenolic resins determines their molecular structure and therefore the physical properties of the resin. An aldehyde: phenol ratio between 0.5:1 and 1:1, preferably 0.5:1 to 0.8:1 and an acid catalyst is used to prepare those phenolic resins generally known as novolaks which are thermoplastic in character. Higher aldehyde:phenol ratios of more than 1:1 to 3:1, and a basic catalyst would give rise to a class of phenolic resins known as resoles, and these are characterised by their ability to be thermally hardened at elevated temperatures.

[0029] Particularly useful phenolic resins in this invention are the condensation products from the interaction between phenol, C-alkyl substituted phenols (such as cresols and p-tert-butyl-phenol), diphenols (such as bisphenol-A) and aldehydes (such as formaldehyde). Dependent on the preparation route for the condensation a range of phenolic materials with varying structures and properties can be formed. Particularly useful in this invention are novolak resins, resole resins and novolak/resole resin mixtures. Most preferred are novolak resins. Examples of suitable novolak resins have the following general structure



[0030] Preferably the composition contains at least 20%, more preferably at least 50%, most preferably at least 70%

of a phenolic resin, or of phenolic resins in total, by weight on total weight of the composition. Other polymers suitable for inclusion in the composition, in admixture with a phenolic resin, include: poly-4-hydroxystyrene; copolymers of 4-hydroxystyrene, for example with 3-methyl-4-hydroxystyrene or 4-methoxystyrene; copolymers of (meth)acrylic acid, for example with styrene; copolymers of maleimide, for example with styrene; hydroxy or carboxy functionalised celluloses; dialkylmaleimide esters; copolymers of maleic anhydride, for example with styrene; and partially hydrolysed polymers of maleic anhydride.

**[0031]** The composition is preferably such that it is patternwise solubilized by heat, during the pattern forming (exposure) process. In broad terms there are three ways in which heat can be patternwise delivered to the composition, in use. These are:-

- direct heat, by which we mean the direct delivery of heat by a heated body, by conduction. For example the composition may be contacted by a heat stylus; or the reverse face of the substrate onto which the composition has been coated may be contacted by a heated body. A heated body may be a heat stylus.
- the use of incident electromagnetic radiation to expose the composition, the electromagnetic radiation being converted to heat, either directly or by a chemical reaction undergone by a component of the composition. The electromagnetic radiation could for example be infra-red, or UV or visible radiation, depending on the composition. Preferably it is infra-red.
- the use of charged-particle radiation, for example electron beam radiation. Clearly, at the fundamental level the charged-particle mode and the electromagnetic mode are convergent; but the distinction is clear at the practical level.

**[0032]** In order to increase the sensitivity of the preferred heat sensitive compositions used in the present invention it is beneficial in embodiments intended for exposure using electromagnetic radiation to include an additional component, namely a radiation absorbing compound capable of absorbing the incident electromagnetic radiation and converting it to heat (hereinafter called a "radiation absorbing compound"). It may also be desirable to include a suitable radiation absorbing compound in embodiments intended for exposure using charged particle radiation.

**[0033]** In preferred compositions intended to require electromagnetic radiation for exposure, the composition may be such that it can be exposed directly by means of a laser. Preferably, such a laser emits radiation at above 450 nm, preferably above 500 nm, more preferably above 600 nm, and especially above 700 nm. Most preferably it emits radiation at above 800 nm. Suitably it emits radiation of wavelength below 1400 nm, preferably below 1200 nm. In such compositions a suitable radiation absorbing compound, to convert the radiation to heat, may usefully be a black body radiation absorber, such as carbon black or graphite. It may be a commercially available pigment such as Heliogen Green as supplied by BASF or Nigrosine Base NG1 as supplied by NH Laboratories Inc or Milori Blue (C.I. Pigment Blue 27) as supplied by Aldrich.

**[0034]** Examples of lasers which can be used to expose compositions suitable for the method of the present invention include semiconductor diode lasers emitting at between 450 nm and 1400 nm, especially between 600 nm and 1100 nm. An example is the Nd YAG laser which emits at 1064 nm, but any laser of sufficient imaging power and whose radiation is absorbed by the composition, can be used.

**[0035]** Preferably the radiation absorbing compound is one whose absorption spectrum is such that absorption is significant at the wavelength output of the radiation source, preferably laser, which is to be used in the patternwise exposure of precursors made by the method of the present invention. Usefully it may be an organic pigment or dye such as phthalocyanine pigment. Alternatively it may be a dye or pigment of the squarylium, merocyanine, cyanine, indolizine, pyrylium or metal dithioline classes.

**[0036]** In preferred compositions intended to require infra-red radiation for patternwise exposure it is preferred that their developer solubility is not increased by incident UV or visible radiation, so making handling of the compositions straightforward. Preferably such compositions do not comprise any UV or visible light sensitive components. However UV or visible light sensitive components which are not activated by UV or visible light due to the presence of other components, such as UV or visible light absorbing dyes or a UV or visible light absorbing topmost layer, may be present in such compositions.

**[0037]** Pigments are generally insoluble in the compositions and so comprise particles therein. Generally they are broad band absorbers, preferably able efficiently to absorb electromagnetic radiation and convert it to heat over a range of wavelengths exceeding 200 nm, preferably exceeding 400 nm. Generally they are not decomposed by the radiation. Generally they have no or insignificant effect on the solubility of the unheated composition, in the developer. In contrast dyes are generally soluble in the compositions. Generally they are narrow band absorbers, typically able efficiently to absorb electromagnetic radiation and convert it to heat only over a range of wavelengths typically not exceeding 100 nm, and so have to be selected having regard to the wavelength of the radiation which is to be used for imaging. Many

dyes have a marked effect on the solubility of the unheated composition in the developer, typically making it much less soluble, and use of such dyes is not within the ambit of the present invention.

**[0038]** Suitably the radiation absorbing compound, when present, constitutes at least 0.25%, preferably at least 0-5%, more preferably at least 1%, most preferably at least 2%, preferably up to 25%, more preferably up to 20%, most preferably up to 15%, of the total weight of the composition. A preferred weight range for the radiation absorbing compound may be expressed as 2-15% of the total weight of the composition. More specifically, in the case of dyes the range may preferably be 0.25-15% of the total weight of the composition, preferably 0.5-8%, whilst in the case of pigments the range may preferably be 1-25%, preferably 2-15%. For pigments, 5-15% may be especially suitable. In each case the figures given are as a percentage of the total weight of the dried composition. There may be more than one radiation absorbing compound. References herein to the proportion of such compound(s) are to their total content.

**[0039]** The compositions used in the invention may contain other ingredients such as stabilising additives, inert colorants, and additional inert polymeric binders as are present in many positive working compositions.

**[0040]** In certain embodiments of the invention an additional layer comprising a radiation absorbing compound can be used. This multiple layer construction can provide routes to high sensitivity as larger quantities of absorber can be used without affecting the function of the image forming layer. In principle any radiation absorbing material which absorbs sufficiently strongly in the desired band can be incorporated or fabricated in a uniform coating. Dyes, metals and pigments (including metal oxides) may be used in the form of vapour deposited layers. Techniques for the formation and use of such films are well known in the art, for example as described in EP 0,652,483.

**[0041]** Said printing form precursor includes a substrate over which said heat sensitive composition is provided. Said substrate may be arranged to be non-ink-accepting. Said substrate may have a hydrophilic surface for use in conventional lithographic printing using a fountain solution or it may have a release surface suitable for use in waterless printing.

**[0042]** Said substrate may comprise a metal layer. Preferred metals include aluminium, zinc and titanium, with aluminium being especially preferred. Said substrate may comprise an alloy of the aforesaid metals. Other alloys that may be used include brass and steel, for example stainless steel.

**[0043]** Said substrate may comprise a non-metal layer. Preferred non-metal layers include layers of plastics, paper or the like. Preferred plastics include polyester, especially polyethylene terephthalate.

**[0044]** Said substrate may be any type of substrate usable in printing. For example, it may comprise a cylinder or, preferably, a plate.

**[0045]** The substrate may be an aluminium plate which has undergone the usual anodic, graining and post-anodic treatments well known in the lithographic art for enabling a radiation sensitive composition to be coated thereon and for the surface of the support to function as a printing background. Another substrate which may be used in the present invention in the context of lithography is a plastics material base or a treated paper base as used in the photographic industry. A particularly useful plastics material base is polyethylene terephthalate which has been treated to render its surface hydrophilic. Also a so-called coated paper which has been corona discharge treated can be used.

**[0046]** In the specification when we state that a composition is developer soluble we mean that it is soluble in a selected developer, to an extent useful in a lithographic printing form development process. When we state that a composition is developer insoluble we mean that it is not soluble in the selected developer, to an extent useful in a lithographic printing form development process.

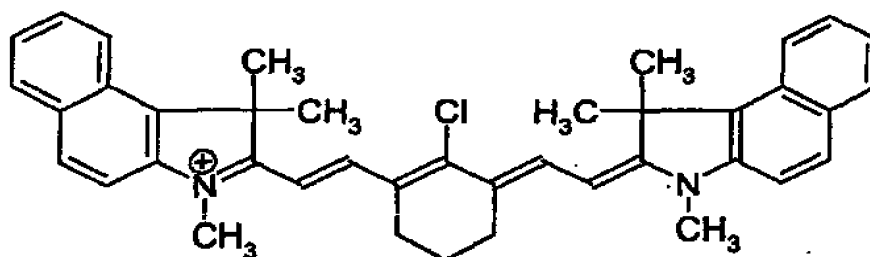
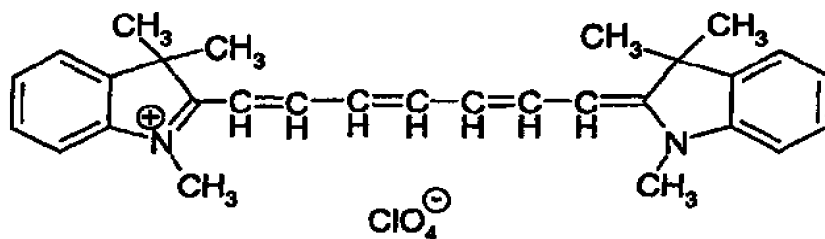
**[0047]** Thus in preferred embodiments a positive working lithographic printing form may be obtained after patternwise exposure and development of a precursor made by the method of the present invention. The developer solubility of the composition after it has been subjected to heat during patternwise exposure is greater than the solubility of the corresponding unexposed composition. In preferred embodiments this solubility differential is increased by means of additional components and/or by resin modification, as described herein. Preferably such measures reduce the solubility of the resin, prior to the patternwise exposure. On subsequent patternwise exposure the exposed areas of the composition are rendered more soluble in the developer, than the unexposed areas. Therefore on patternwise exposure there is a change in the solubility differential of the unexposed composition and of the exposed composition. Thus in the exposed areas the composition is dissolved, to form the pattern.

**[0048]** The coated printing form precursor produced by the method of the invention may in use be patternwise heated indirectly by exposure to a short duration of high intensity radiation transmitted or reflected from the background areas of a graphic original located in contact with the recording material.

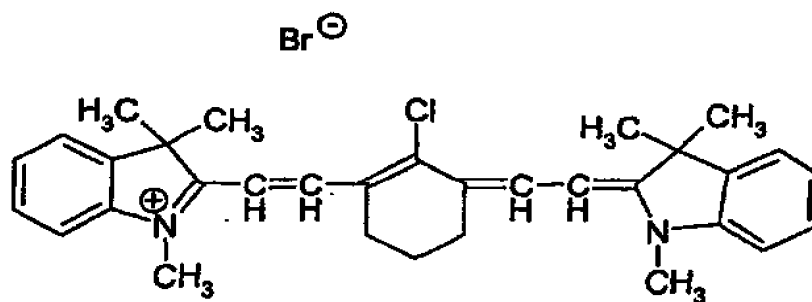
**[0049]** The developer is dependent on the nature of the polymeric substance, but is preferably an aqueous developer. Common components of aqueous developers are surfactants, chelating agents such as salts of ethylenediamine tetraacetic acid, organic solvents such as benzyl alcohol, and alkaline components such as inorganic metasilicates, organic metasilicates, hydroxides or bicarbonates.

**[0050]** Preferably an aqueous developer is an alkaline developer containing inorganic or organic metasilicates.

**[0051]** As indicated above preferred compositions to which the method of the present invention may advantageously be applied contain infra-red absorbing compounds. Examples of suitable infra-red absorbing compounds are:-



and KF654B PINA as supplied by Riedel de Haen UK, Middlesex, England, believed to have the structure:



**[0052]** We believe the present invention can be applied with benefit to any precursor whose composition comprises a phenolic resin; but especially to such compositions arranged such that patternwise exposure entails the delivery of heat to selected areas of the precursor.

**[0053]** Thus the present invention is applicable to the heat sensitive phenolic resin systems described in GB 1245924, incorporated herein by reference, these being simple systems comprising a phenolic resin and a radiation absorber, preferably a black body absorber, for example carbon black or Milori Blue, without further components to enhance the solubility differential of the composition, on patternwise exposure.

**[0054]** The present invention is also applicable to the systems described in US 5491046, incorporated herein by reference, whose heat sensitive compositions comprise latent Bronsted acids. These are negative working and positive working; the latter being of interest in the context of the present invention.

**[0055]** In the systems of US 5491046 it is said that the said heat sensitive compositions may comprise a resole resin, a novolak resin, a latent Bronsted acid and an infra-red absorber, said compositions being arranged to be sensitive to both ultraviolet and infra-red radiation.

[0056] Optionally terephthalaldehyde may be included as a speed enhancing agent.

[0057] Optionally 3,4,5-trimethoxybenzoic acid may be included, to enhance image/non-image contrast.

[0058] Said resole resin may be prepared from bis-phenol A and formaldehyde. Said novolak resin may be prepared from m-cresol and formaldehyde.

[0059] The term "latent Bronsted acid" refers to a precursor which forms a Bronsted acid by decomposition. Typical examples of Bronsted acids which are suitable for this purpose are trifluoromethane sulphonic acid and hexafluorophosphoric acid.

[0060] Ionic latent Bronsted acids are also suitable. Examples of these include onium salts, in particular iodonium, sulfonium, phosphonium, selenonium, diazonium and arsonium salts. Specific examples of particularly useful onium salts include: diphenyliodonium hexafluorophosphate, triphenylsulfonium hexafluoroantimonate, phenylmethyl-orthocyanobenzylsulfonium trifluoromethane sulfonate, and 2-methoxy-4-aminophenyl diazonium hexafluorophosphate.

[0061] Non-ionic latent Bronsted acids are also suitable. Examples of these include compounds of the formula:

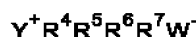


and



wherein X is Cl, Br, F, or  $CF_2SO_3$  and  $R^3$  is an aromatic group, an aliphatic group or a combination of aromatic and aliphatic groups.

[0062] Useful ionic latent Bronsted acids include those represented by the formula:



[0063] When Y is iodine then  $R^6$  and  $R^7$  are electron lone pairs and  $R^4$  and  $R^5$  are aryl or substituted aryl groups. When Y is S or Se then  $R^7$  is an electron lone pair and  $R^4$ ,  $R^5$  and  $R^6$  can be an aryl group, a substituted aryl group, an aliphatic group or a substituted aliphatic group. When Y is P or As, then  $R^7$  can be an aryl group, a substituted aryl group, an aliphatic group or a substituted aliphatic group. W can be  $BF_4$ ,  $CF_3SO_3$ ,  $SbF_6$ ,  $CCl_3CO_2$ ,  $ClO_4$ ,  $AsF_6$ ,  $PF_6$ , or any corresponding acid whose pH is less than three.

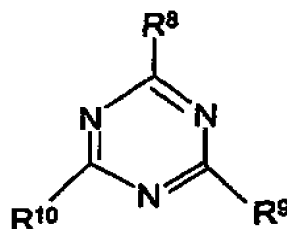
[0064] Any of the onium salts described in U.S. Pat. No. 4,708,925, incorporated herein by reference, can be utilized as the latent Bronsted acid.

[0065] Use of diazonium salts as latent Bronsted acids is particularly preferred. They provide equivalent sensitivity to other latent Bronsted acids in the infra-red region and higher sensitivity in the ultraviolet region.

[0066] An additional class of useful latent Bronsted acids are the haloalkyl-substituted s-triazines. The haloalkyl-substituted s-triazines are well known photolytic acid generators. Use of these compounds for this purpose is described, for example, in U.S. Pat. No 3,779,778, incorporated herein by reference.

[0067] Preferred haloalkyl-substituted s-triazines for use in this invention are compounds of the formula:



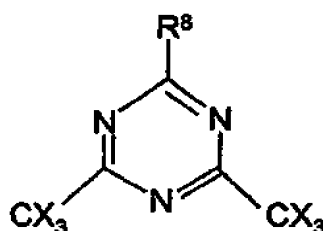


wherein  $\text{R}^8$  is a substituted or unsubstituted aliphatic or aromatic radical and  $\text{R}^9$  and  $\text{R}^{10}$  are, independently, haloalkyl groups.

[0068] In the above formula, it is especially preferred that  $\text{R}^9$  and  $\text{R}^{10}$  are haloalkyl groups of 1 to 4 carbon atoms.

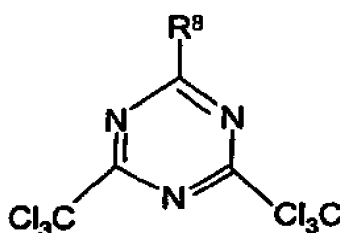
[0069]  $\text{R}^8$  can include any substituent which does not adversely affect the photolytic acid-generating capability of the s-triazine compound. Such substituents include alkyl groups and alkoxy groups.

[0070] Particularly preferred haloalkyl-substituted s-triazines are compounds of the formula:



wherein  $\text{R}^8$  is a substituted or unsubstituted aliphatic or aromatic radical and each X preferably is, independently, a halogen atom.

[0071] The most preferred haloalkyl-substituted s-triazines compounds for use in these embodiments are of the formula:



wherein  $\text{R}^8$  is an aryl group of 6 to 15 carbon atoms, such as, for example, phenyl or naphthyl.

[0072] The infra-red absorber may be as previously described.

[0073] The present invention is also applicable to the similar systems described in US patents 5466557, 5372915 and 5372907, related to US 5491046.

[0074] We also believe the present invention to be applicable to the phenolic resin systems described in US 4708925, comprising an onium salt. Suitable onium salts include iodonium, sulphonium, bromonium, chloronium, oxysulphonium, sulfoxonium, selenonium, telluronium, phosphonium and arsonium salts. Preferably, an iodonium, sulphonium or oxysulphonium salt is present.

[0075] The onium salt is generally included in the composition in an amount in the range from 1 to 40% by weight of the total weight of phenolic resin and onium salt. The amount of onium salt is selected to provide the desired solubility differential between the unexposed and exposed compositions. It has been found that resole resins normally require

the onium salt in an amount of at least 5% by weight of the total weight of phenolic resin and onium salt in order to ensure a satisfactory solubility differential. Generally, compositions employing resole resins will include at least 7% by weight, of onium salt. It is possible to achieve a satisfactory solubility differential in compositions containing novolak resins containing smaller amounts of onium salt, generally in the range 1 to 40% by weight of onium salt. Suitably a further component of such compositions is a spectral sensitiser in an amount of up to 10% by weight of the composition, selected from one of the following classes: diphenylmethane, xanthene, acridine, methine and polymethine, (including oxonol, cyanine and merocyanine) dye, thiazole, thiazine, azine, aminoketone, porphyrin, coloured aromatic polycyclic hydrocarbon, p-substituted aminostyryl compound, aminotriazyl methane, polyarylene, polyarylpolymethine, 2,5-diphenylisobenzofuran, 2,5-diarylcyclopentadiene, diarylfuran, diarylthiofuran, diarylpyrrole, polyarylphenylene, coumarin and polyaryl-2-pyrazoline. Further information on these compositions is given in US 4708925.

[0076] We will now describe separately, in detail, five of our new systems which are the subject of patent applications to which the method of the present invention may be applied.

[0077] The method of the present invention as described above may be applied to our novel compositions as described in our patent application WO 97/39894.

[0078] The method of the present invention as defined above may be applied to our novel compositions as described in our patent application WO 98/01795.

[0079] The method of the present invention may be applied to compositions described in WO 98/01796.

[0080] The method of the present invention as defined above may be applied to the positive working aspects of our novel compositions as described in WO 98/31544.

[0081] The methods of the present invention as defined above may be applied to our novel compositions as described in WO 99/21725.

[0082] In accordance with a second aspect of the present invention there is provided a printing form precursor manufactured by a method as previously defined. The coating preferably comprises a phenolic resin composition which is to be patternwise exposed by heat. Many examples are given above.

[0083] In accordance with a third aspect of the invention there is provided a method of producing a printing form, from a printing form precursor of the second aspect, comprising an exposure step of exposing selected areas of the composition such as to render them developer soluble, followed by development in a developer to remove said selected areas. The exposure preferably entails heating the selected areas. The heating of selected areas may be effected in the different ways applicable to the different compositions, as described above.

[0084] In accordance with a fourth aspect of the invention there is provided a printing form produced by the method of the third invention.

[0085] The following Examples more particularly serve to illustrate various embodiments of the present invention described hereinabove.

### **Starting Materials**

[0086] The following are referred to hereinafter.

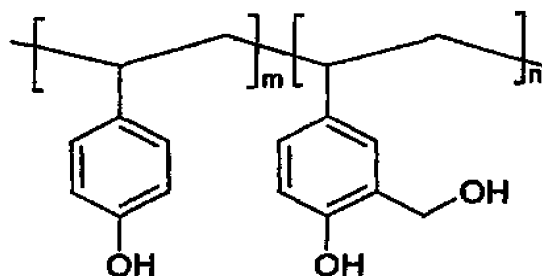
Resin A: LB6564 - a 1:1 phenol/cresol novolak resin supplied by Bakelite, UK.

Resin B: LB744 - a cresol novolak resin supplied by Bakelite.

Resin C: LB6564 phenolic resin modified by simple reaction with p-toluene sulphonyl chloride as follows.

1. Dissolve LB 6564 (25.0 g) resin (Resin A) in 61.8 g of 2-methoxyethanol.
2. Immerse a three-necked 500 ml round-bottomed flask in a water bath placed on a hot plate/stirrer. Attach a stirrer gland, stirring rod and a thermometer to the flask.
3. Place the resin solution into the flask and begin rapid stirring.
4. Slowly add 25.6 g of distilled water drop-wise keeping precipitation to a minimum.
5. Add sodium hydrogen carbonate (4.3 g) to the flask. Not all of the solid will dissolve.
6. Slowly add the acid chloride (1.18 g) with vigorous stirring.
7. Warm the reaction mixture for 6 hours at 40°C with stirring.
8. After 6 hours, remove the flask from the water bath and allow to cool (about 30 mins).
9. Prepare a dilute solution by adding 8.6 g of 1.18 s.g. hydrochloric acid to 354 g of distilled water.
10. Slowly precipitate the esterified resin drop-wise into the dilute acid with stirring.
11. Filter and wash the precipitate by re-slurrying in distilled water at least three times if possible until the pH of the filtrate reaches 6.0.
12. Dry the precipitate in a vacuum oven at 40°C. 75% yield. Identity confirmed by IR spectroscopy.

Resin D: Methylol polyvinyl phenol, believed to have the structure:



$$m : n = 77 : 23$$

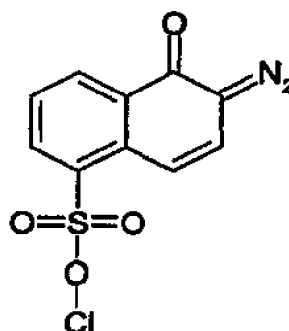
Resin E: Uravar FN6, an alkyl phenolic resole resin as supplied by DSM Resins UK, South Wirral, UK.

Resin F: LG 724, a phenol novolak resin supplied by Bakelite, UK.

Resin G: LB6564 phenolic resin modified by simple reaction with 214-NQD chloride as follows.

1. Dissolve LB 6564 (25.0 g) resin (Resin A) in 61.8 g of 2-methoxyethanol.
2. Immerse a three-necked 500 ml round-bottomed flask in a water bath placed on a hot plate/stirrer. Attach a stirrer gland, stirring rod and a thermometer to the flask.
3. Place the resin solution into the flask and begin rapid stirring.
4. Slowly add 25.6 g of distilled water drop-wise keeping precipitation to a minimum.
5. Add sodium hydrogen carbonate (4.3 g) to the flask. Not all of the solid will dissolve.
6. Slowly add the acid chloride (4.5 g) with vigorous stirring.
7. Warm the reaction mixture for 6 hours at 40°C with stirring.
8. After 6 hours, remove the flask from the water bath and allow to cool (about 30 mins).
9. Prepare a dilute solution by adding 8.6 g of 1.18 s.g. hydrochloric acid to 354 g of distilled water.
10. Slowly precipitate the esterified resin drop-wise into the dilute acid with stirring.
11. Filter and wash the precipitate by re-slurrying in distilled water at least three times if possible until the pH of the filtrate reaches 6.0.
12. Dry the precipitate in a vacuum oven at 40°C. 75% yield. Identity confirmed by IR spectroscopy.

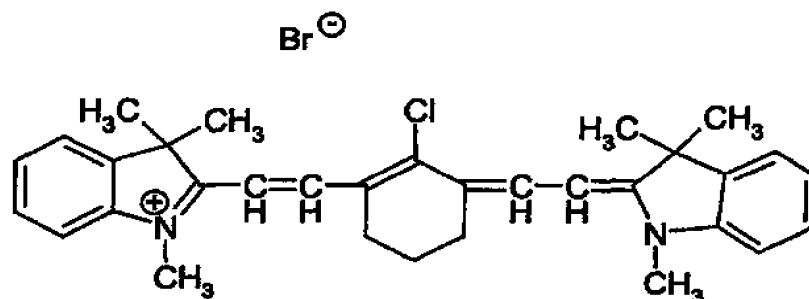
(214-NQD chloride - the compound



supplied by A.H. Marks, Bradford, UK).

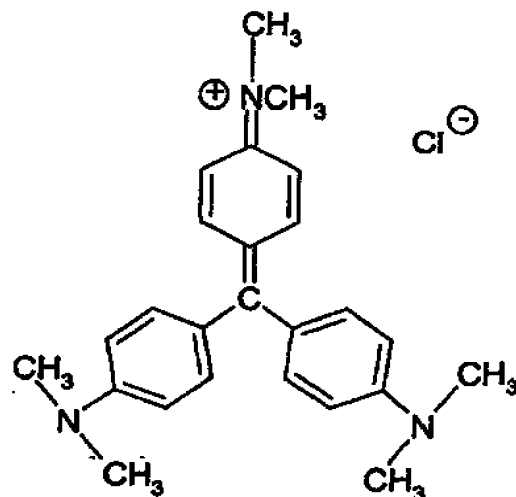
Resin H: Durite PD-494A, a cresylic resin supplied by Borden, Columbus, Ohio, USA.

Dye A - KF654B PINA as supplied by Riedel de Haan UK, Middlesex, UK, believed to have the structure:



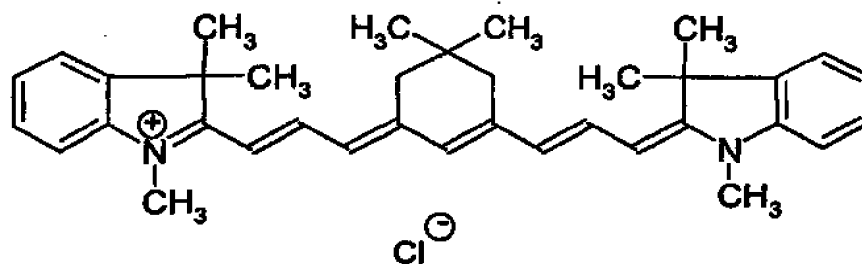
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Dye B - crystal violet (basic violet 3, C.I. 42555, Gentian Violet) as supplied by Aldrich Chemical Company, Dorset, UK, having the structure:

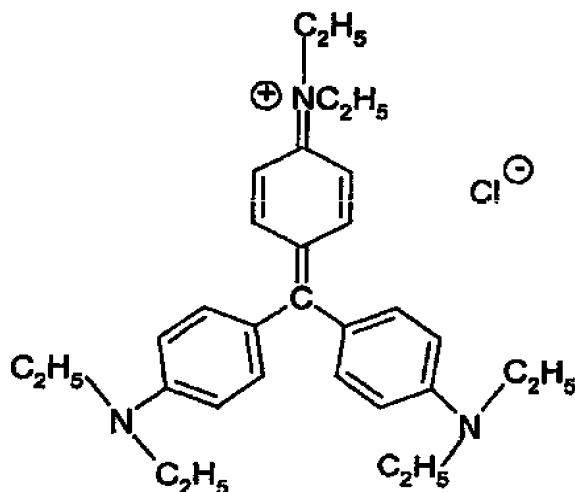


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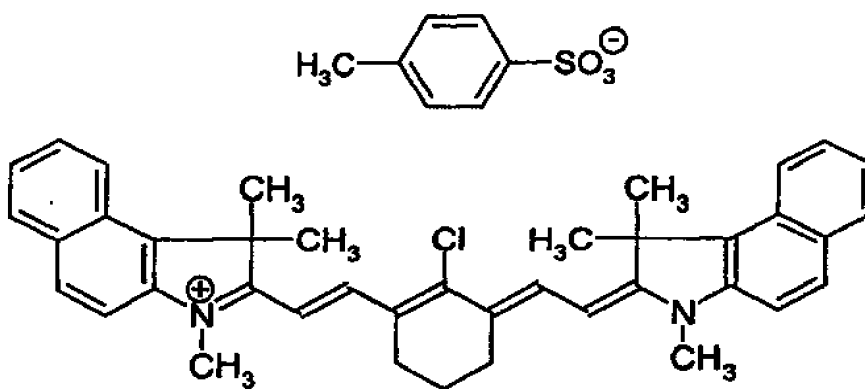
Dye C - I-I-62L as supplied by H.W. Sands of Jupiter, Florida, USA, believed to have the structure:



Dye D - Ethyl violet (Basic Violet 4, C.I. 42600) as supplied by Aldrich Chemical Company, Dorset, UK, having the structure:

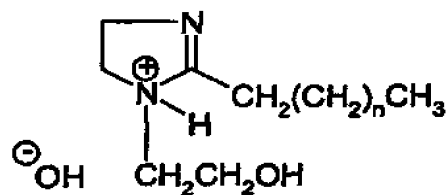


Dye E - SDB7047, having the structure:

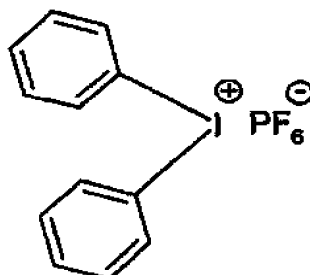


as supplied by H.W. Sands, Jupiter, Florida, USA.

Monazoline C - a cocyl imidazoline, supplied by Mona Industries Inc, New Jersey, USA, believed to have the structure:



Acid Generator A - diphenyliodonium hexafluorophosphate,



supplied by Avocado Research Chemicals Ltd, Heysham, Lancashire, UK.

Silikophen P50X - a phenyl methyl siloxane as supplied by Tego Chemie Service GmbH of Essen, Germany.

Carbon black FW2 - a channel type carbon black as supplied by Degussa, of Macclesfield, UK.

Prussian blue - ferric ferrocyanide, CI pigment Blue 27, supplied by Aldrich.

Developer A - 14% wt sodium metasilicate pentahydrate in water.

Developer B - 7% wt sodium metasilicate pentahydrate in water.

Substrate A - 0.3 mm sheet aluminium electrograined and anodised and post-anodically treated with an aqueous solution of an inorganic phosphate.

### **Exposure Test Methods**

**[0087]** Printing plate precursors made according to the Examples 1 to 11 below were imaged in a commercially available image setter, the Trendsetter 3244 using Procomm Plus software, operating at a wavelength of 830 nm at powers of up to 8 W and supplied by Creo Products Inc. of Burnaby, Canada.

**[0088]** For Examples 12 to 14 below the coated substrate to be imaged was cut into a circle of 105 mm diameter and placed on a disc that could be rotated at a constant speed of 2500 revolutions per minute. Adjacent to the spinning disc a translating table held the source of the laser beam so that the laser beam impinged perpendicularly onto the coated substrate, while the translating table moved the laser beam radially in a linear fashion with respect to the spinning disc. The exposed image was in the form of a spiral whereby the image in the centre of the spiral represented slow laser scanning speed and long exposure time and the outer edge of the spiral represented fast scanning and short exposure time.

**[0089]** The laser used was a single mode 830 nm wavelength 200 mW laser diode which was focused to a 10 micron spot. The laser power supply was a stabilised constant current source.

### **Example 1**

**[0090]** The coating formulation for example 1, as described below, was prepared as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The coating solutions were coated onto Substrate A by means of a wire wound bar. The solution concentrations were selected to provide the specified dry film compositions with a coating weight of 2.5 gm<sup>-2</sup> after thorough drying at 100°C for 3 minutes in a Mathis labdryer oven as supplied by Werner Mathis AG, Germany.

Example 1	
Component	Parts by Weight
Resin A	70
Resin B	20
Dye A	2

(continued)

	<b>Example 1</b>
<b>Component</b>	<b>Parts by Weight</b>
Dye B	2
Silikophen P50X	6

[0091] Individual plate samples were then covered with interleaving (a polythene coated paper No. 22, 6 gm<sup>-2</sup> as supplied by Samuel Grant, U.K.), wrapped in paper (unbleached, unglazed Kraft 90 gm<sup>-2</sup>, coated with matt black low density polythene 20 gm<sup>-2</sup> as supplied by Samuel Grant, U.K.) and placed in an Gallenkamp hotbox oven with fan, size 2, as supplied by Sanyo Gallenkamp plc of Leicester, U.K., at 50°C for 0, 2, 3, 5 and 12 days respectively.

[0092] The resulting heat treated plates were imaged using the Creo Trendsetter at 7 watts with a 50% screen image at imaging energy densities of 120, 140, 160, 180, 200 and 220 mJcm<sup>-2</sup>. The plates were developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 1000 mm min<sup>-1</sup>. Finally, images produced were evaluated visually and the energy required to produce a 50% imaged plate was recorded (mJcm<sup>-2</sup>).

	<b>Number of days plates having resided in oven at 50°C</b>				
	0	2	3	5	12
Energy required to produce 50% image/ mJcm <sup>-2</sup>	No coating retained	140-160	160-180	160-180	160-180

**Example 2**

[0093] A coating formulation for example 2 as described below, was prepared as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The formulation was coated as described in example 1 onto Substrate A to provide the specified dry film composition with a coating weight of 2.0 gm<sup>-2</sup>, after thorough drying at 130°C for 80 seconds in a Mathis labdryer oven.

	<b>Example 2</b>
<b>Component</b>	<b>Parts by Weight</b>
Resin A	90
Dye A	4
Dye B	3
Silikophen P50X	3

[0094] Individual plate samples were then wrapped in paper (unbleached, unglazed Kraft 90 gm<sup>-2</sup>, coated with matt black low density polythene 20 gm<sup>-2</sup>) and placed in a Gallenkamp hotbox oven with fan, size 2, under the following conditions.

<b>Temperature/°C</b>	<b>Time</b>
50	1, 20, 28, 48 hours
85	0.25, 0.5, 1, 2, 24, 48 hours
110	0.25, 0.5, 0.75, 25, 48 hours
140	2, 4, 6, 8, 10, 12, 300, 600 minutes

[0095] The resulting heat treated plates were then imaged at 8 watts with a 50% screen image using the Creo Trendsetter as described previously at an imaging energy density of 200 mJcm<sup>-2</sup>. The plates were then developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 700 mm min<sup>-1</sup>. Finally images produced were read using a Tobias plate check densitometer as supplied by Tobias Associates

Inc. of Ivyland, Pennsylvania, U.S.A. and are expressed in the following table.

**Densitometer readings for example 2**

**5 [0096]**

**10**

**15**

**20**

**25**

**30**

**35**

**40**

**45**

**50**

**55**



20 25 30 35 40 45 50 55

	Time of heat treatment (hours)												
	0.03	0.07	0.1	0.13	0.17	0.2	0.3	0.5	0.8	1	2	5	10
50°C										45%			
85°C							43%	46%		47%	50%		
110°C							36%	42%	43%				
140°C	36%	52%	65%	70%	71%	78%						100%	100%

**Example 3**

[0097] The coating formulation of example 1 was prepared as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The formulation was reverse roller coated onto Substrate A. The solution concentration was selected to provide the specified dry film composition with a coating weight of 2.5 gm<sup>-2</sup>, after thorough drying at 140°C for 30 seconds in an air flotation oven.

[0098] Plates were individually wrapped in paper (unbleached, unglazed Kraft 90 gm<sup>-2</sup>, coating with matt black low density polythene 20 gm<sup>-2</sup>) and placed in a Gallenkamp hotbox oven with fan, size 2 at 50°C for 0, 17, 24 and 70 hours. The resulting heat treated plates were then imaged at 8 watts with a 50% screen image using the Creo Trendsetter as described previously at an imaging energy density of 180 mJcm<sup>-2</sup>. The plates were developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 1000 mm min<sup>-1</sup>. Finally, images produced were read using the Tobias plate check densitometer.

[0099] Densitometer readings of 50% screen images exposed by the Creo Trendsetter were as follows.

	Number of hours plates have resided in oven			
	0	17	24	70
Densitometer Reading	0%	47%	52%	52%

**Example 4**

[0100] In this example both the coating and the heat treatment steps used factory rather than laboratory equipment.

[0101] The coating formulation of example 1 was prepared as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The formulation was reverse roller coated onto Substrate A. The solution concentration was selected to provide the specified dry film composition with a coating weight of 2.5 gm<sup>-2</sup>, after thorough drying at 110°C for 75 seconds in a hot air displacement oven.

[0102] Plates were then placed in a hot air displacement oven at 50°C for 49.5 hours. The resulting heat treated plates were then imaged at 8 watts with a 50% screen image using the Creo Trendsetter as described previously at an imaging energy density of 120, 140, 160, 180, 200 and 220 mJcm<sup>-2</sup>. The plates were then developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 1000 mm min<sup>-1</sup>.

[0103] Finally, images produced were evaluated visually and the energy required to produce a 50% image was recorded as 180 mJcm<sup>-2</sup>.

**Examples 5-8**

[0104] Coating formulations set out below were prepared as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The formulations were coated as described in example 1 onto Substrate A to provide the specified dry film composition with a coating weight of 2.0 gm<sup>-2</sup> after thorough drying at 100°C for 3 minutes in a Mathis labdryer oven.

	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Resin A	93.5	92.5	91	92
Monazoline C	1	1	2.5	0
Dye C	2	3	3	4
Dye D	0.5	0.5	0.5	1
Silikophen P50X	3	3	3	3

[0105] Plates were individually covered with interleaving (a polythene coated paper 6 gm<sup>-2</sup>), wrapped in paper (unbleached, unglazed Kraft 90 gm<sup>-2</sup>, coated with matt black low density polythene 20 gm<sup>-2</sup>) and placed in a Gallenkamp hotbox oven with fan, size 2 under the following conditions:

Temperature (°C)	Residence time (days)
50	0, 2, 5

[0106] The resulting heat treated plates were then imaged at 8 watts with a 50% screen image using the Creo

Trendsetter as described previously at an imaging energy density of 500 mJcm<sup>-2</sup>. The plates were developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 700 mm min<sup>-1</sup>. Finally, images produced were read using the Tobias plate check densitometer.

[0107] Densitometer readings of 50% images exposed by the Creo Trendsetter were as follows:

	Number of hours plates have resided in oven at 50°C		
	0	2	5
Example			
5	0	52	51
6	18	52	51
7	42	57	56
8	14	50	50

#### **Example 9**

[0108] A coating formulation identical to that of example 1 was prepared as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The formulations were coated onto Substrate A as described in example 1 to provide the specified dry film composition with a coating weight of 2.0 gm<sup>-2</sup> after thorough drying at 130°C for 80 seconds in a Mathis labdryer oven.

[0109] Plate samples were then either:

1. covered with interleaving (a polythene coated paper, 6 gm<sup>-2</sup>), and then wrapped as a 13 plate packet in paper (unbleached, unglazed Kraft 90 gm<sup>-2</sup>, coated with matt black low density polythene 20 gm<sup>-2</sup>)

or 2. left un-interleaved but wrapped as a 13 plate packet in paper (unbleached, unglazed Kraft 90 gm<sup>-2</sup>, coated with matt black low density polythene 20 gm<sup>-2</sup>) and placed in a Gallenkamp hotbox oven with fan, size 2, for various times (0 to 80 hours) at 50°C. The resulting heat treated plates were then imaged with 50% screen images using the Creo Trendsetter as described previously at an imaging energy density of 200 mJcm<sup>-2</sup>. The plates were developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 700 mm min<sup>-1</sup>. Finally, images produced were read using the Tobias plate check densitometer. The results are expressed in the table below.

#### **Densitometer readings for example 9**

[0110]

	Time of heat treatment (hours)										
	4	6	9	18	24	28	32	45	48	50	52
not interleaved	20%	32%		47%	47%	47%		49%			
interleaved		34%	42%		48%		50%		50%	50%	50%

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20

**Example 10**

[0111] A coating formulation set out below was prepared as described in example 1 as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The formulation was coated onto Substrate A as described in example 1 to provide the specified dry film composition with a coating weight of 2.0 gm<sup>-2</sup> after thorough drying at 100°C for three minutes in a Mathis labdryer oven.

<b>Example 10</b>	
Component	Parts by Weight
Resin C	96
Dye A	2
Dye B	2

[0112] Individual plate samples were then covered with interleaving (a polythene coated paper 6 gm<sup>-2</sup>), wrapped in paper (unbleached, unglazed Kraft 90 gm<sup>-2</sup>, coated with matt black low density polythene 20 gm<sup>-2</sup>) and placed in a Gallenkamp hotbox oven with fan, size 2, for various times (0 to 17 days) and temperatures (room temperature to 50°C). The resulting heat treated plates were then imaged with 50% screen images using the Creo Trendsetter as described previously at an imaging energy density of 200 mJcm<sup>-2</sup>. The plates were developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 500 and 1500 mm min<sup>-1</sup>. Finally, images produced were read using the Tobias plate check densitomer. The densitometer readings are given in the tables below.

**Results for plates heat treated at 40°C**

[0113]

		Number of days plates have resided in oven				
		0	4	6	8	10
Processing Speed mm min <sup>-1</sup>	500	0%	51%	52%	64%	65%
	1500	0%	71%	73%	72%	67%

**Results for plates heat treated at 50°C**

[0114]

		Number of days plates have resided in oven				
		0	1	2	3	10
Processing Speed mm min <sup>-1</sup>	500	0%	53%	47%	47%	68%
	1500	0%	72%	70%	67%	83%

**Results for plates treated at room temperature**

[0115]

		Number of days plates have resided in oven			
		0	5	12	17
Processing Speed mm min <sup>-1</sup>	500	0%	10%	22%	41%
	1500	0%	18%	47%	60%

[0116] It should be noted that example 10 gives the results of preliminary tests on the compositions containing Resin C and the heat treatment conditions were far from optimised. However we believe the results show that a temperature

above room temperature will be required to get good stability, and that heat treatment at a temperature of at least 40°C for 1-6 days is likely to yield adequately stable compositions.

#### **Example 11**

[0117] The coating formulation for example 11 was ball milled together for 24 hours in 1-methoxypropan-2-ol. The coating solution was coated onto Substrate A by means of a wire wound bar. The solution concentration was selected to provide the specified dry film composition with a coating weight of 2.5 gm<sup>-2</sup> after thorough drying at 100°C for 3 minutes in a Mathis lab dryer oven.

Example 11	
Component	Parts by Weight
FW2	12
Resin B	88

[0118] Individual plate samples were then wrapped in paper (unbleached, unglazed Kraft 90 gm<sup>-2</sup>, coated with matt black low density polyethylene 20 gm<sup>-2</sup>) and

- 1) stored at room temperature for 0, 1, 2, and 4 days or
- 2) placed in a Gallenkamp hotbox oven with fan, size 2 at 55°C for 0, 1, 2 and 4 days.

[0119] The resulting heat treated plates were imaged using the Creo Trendsetter at 7 watts with a 50% screen image at imaging energy densities of 150, 200, 250 and 300 mJcm<sup>-2</sup>. The plates were developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 750 mm min<sup>-1</sup>. Finally, images produced were evaluated visually and the energy required to produce a 50% image was recorded.

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	Imaging Energy Density/mJcm <sup>-2</sup>											
	150				200				250			
Age of plate/days	0	1	2	4	0	1	2	4	0	1	2	
Plates placed in oven	5%	33%	35%	47%	0%	27%	30%	44%	0%	26%	32%	
Plates stored at room temp.	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	

**Examples 12 to 14**

**[0120]** Coating formulations were prepared as described in example 1 as solutions in 1-methoxypropan-2-ol/dimethylformamide 50:50 (w:w) for examples 12 and 13 and as solutions in 1-methoxypropan-2-ol for Example 14. The formulations were coated as previously described onto Substrate A to provide the specified dry film composition with coating weights of 1.2 gm<sup>-2</sup> for examples 12 and 13, and a coating weight of 2.5 gm<sup>-2</sup> for example 14, after thorough drying at 130°C for 80 seconds in a Mathis labdryer oven.

	Example		
	12	13	14
Component	Parts by Weight		
Resin A	42	42	
Resin D	42		
Acid Generator A	12	12	
Dye E	4	4	
Resin E		42	
Resin F			20
Dye A			2
Dye B			2
Resin G			76

- 1) placed in a Gallenkamp hotbox oven with fan, size 2, at 50°C for 2 days or
- 2) stored at room temperature for 2 days.

**[0121]** The plates were then imaged using the rotating disc apparatus as described previously. The exposed plates were developed by immersing in developer A at 20°C for example 13 and developer B at 20°C for examples 12 and 14, which removed the imaged coating areas leaving a spiral image. The immersion time required to leave an image having an imaging energy density of 120 mJcm<sup>-2</sup> are given in the first column of the table below.

**[0122]** In addition, plate samples of example 12 were tested for developability by immersing in developer B at 20°C for an appropriate time and plate samples of examples 13 and 14 were tested for developability by immersing in developer A at 35°C for an appropriate time. The second column in the following table lists the results of these simple developability tests for the compositions.

		Immersion time required/ seconds	Time to fully remove coating/ seconds
Example 12	Samples placed in oven	60	35
	Samples stored at room temperature	30	3
Example 13	Samples placed in oven	120	120
	Samples stored at room temperature	60	90
Example 14	Samples placed in oven	40	45
	Samples stored at room temperature	30	15

**[0123]** For example 15 Prussian Blue and resin B (at a ratio of 1:4, w:w) were ball milled together for four days such that the dispersed mill-base had a solids content of 30% in 1-methoxy-2-propyl acetate and a particle size of <10



microns as determined by grind gauge.

[0124] For example 16, Prussian blue and resin H were ball milled as described above.

[0125] For example 17, Carbon black FW2 and resin B were ball milled as described above.

[0126] The coating formulations then for examples 15-17 were prepared as solutions in 1-methoxy propan-2-ol : 1-methoxy-2-propyl acetate (50:50 w:w).

[0127] The coating solutions were coated onto Substrate A by means of a wire wound bar.

	Examples		
	15	16	17
Component			
Resin A	48		
Resin B	40		88
Resin C		88	
Prussian Blue	12	12	
Carbon Black FW2			12

[0128] Individual plate samples were then covered with interleaving (a polythene coated paper No. 22, 6 gm<sup>-2</sup> as supplied by Samuel Grant UK), wrapped in paper (unbleached, unglazed Kraft 90 gm<sup>-2</sup>), coated with matt black low density polythene (20 gm<sup>-2</sup> as supplied by Samuel Grant, UK), and placed in a Gallenkamp hotbox oven with fan, size 2, as supplied by Sanyo Gallenkamp, at 55°C for 4 days.

[0129] Plate samples were then imaged on the Trendsetter 3244, using the internal test pattern, plot 0 (50% screen) at 10W, 200 mJcm<sup>-2</sup>, 127 rpm.

[0130] The exposed samples were then processed by immersing in developer B at 21°C for an appropriate time as described below. Other samples were processed using a Horsell Mercury Mark V processor filled with Developer A at 22.5°C and having a plate speed of 1500 mm/min. The images (written as 50% dots) were measured using a Tobias plate check densitometer as supplied by Tobias Associates Inc, of Ivyland, Pennsylvania, USA.

	Processing by Immersion		Processing using Mercury Mark V
	Time/seconds	Written 50% dots	Written 50% dots
Example			
15	15	52%	47%
16	30	46%	67%
17	15	47%	52%

[0131] In the specification we refer in various places to UV, infra-red and visible radiation. A person skilled in the art will be aware of the typical wavelength ranges of these radiations. However, for the avoidance of any doubt, UV radiation typically has a wavelength range not exceeding about 450 nm (by which we mean insubstantial above 450 nm). Visible radiation has a wavelength range of about 400 to 700 nm. Infra-red radiation typically has a wavelength range in excess of 600 nm, the boundaries between UV and visible radiation, and between infra-red and visible radiation, not being sharp ones.

## Claims

1. A method of manufacturing a printing form precursor which comprises a coating on a substrate, the coating comprising a positive working composition which comprises a phenolic resin, wherein the method of manufacturing comprises the application of the composition in a solvent to the substrate, the drying of the composition, and the subsequent heat treatment of the coated substrate, and wherein the heat treatment is carried out for at least 4 hours.
2. A method as claimed in Claim 1, wherein the heat treatment is carried out at a temperature in the range 40-90°C.
3. A method as claimed in any preceding claim, wherein the drying of the composition is carried out by subjecting

the substrate carrying the composition in a solvent to a temperature exceeding the temperature selected for the heat treatment, and for a period of time less than that selected for the heat treatment.

- 5 4. A method as claimed in any preceding claim, wherein the composition is such that its solubility in a developer is not increased by incident UV radiation.
- 10 5. A method as claimed in any preceding claim, wherein said composition is such that it may be patternwise exposed by direct heat, or by charged particle radiation or electromagnetic radiation, in each case converted to heat by the coating.
- 15 6. A method as claimed in Claim 5, wherein the composition is such that it may be patternwise exposed by electromagnetic radiation of wavelength entirely or predominantly in the range 450 to 1400 nm, wherein the coating includes a radiation absorbing compound able to absorb said radiation and convert it to heat.
- 20 7. A method as claimed in any preceding claim, wherein the composition comprises an aqueous developer soluble phenolic resin and a compound which reduces the aqueous developer solubility of the phenolic resin, wherein the aqueous developer solubility of the composition is increased on heating and the aqueous developer solubility of the composition is not increased by incident UV radiation.
- 25 8. A method as claimed in any of Claims 1 to 6, wherein the phenolic resin meets at least one of the following definitions:
  - it has functional groups Q thereon, such that the functionalised phenolic resin has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter, wherein the functional groups Q do not comprise a naphthoquinone diazide or a benzoquinone diazide group;
  - 30 - it has functional groups Q thereon, such that the functionalised phenolic resin has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter, wherein the functional groups Q do not contain a diazide group;
  - it has functional groups Q thereon, such that the functionalised phenolic resin has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter, wherein the functional groups are not chemically decomposed on exposure to said radiation;
  - 35 - it has functional groups Q thereon, such that the functionalised phenolic resin has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter, wherein the functional groups Q do not comprise acid groups or acid generating groups, in each case protected by labile protective groups removed on exposure to said radiation;
  - 40 - it has functional groups Q thereon, such that the functionalised phenolic resin has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter, wherein the functional groups Q are not additionally primarily responsible for the absorption of said radiation;
  - 45 - it has functional groups Q thereon, such that the functionalised phenolic resin has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter, wherein there is hydrogen bonding between said functional groups Q and other groups of the same molecule or other molecule(s) of the polymeric substance.
- 50 9. A method as claimed in Claims 8, wherein the functional groups Q are selected from groups which comprise amino, monoalkylamino, dialkylamino, amido, monoalkylamido, dialkylamido, chloro, fluoro, carbonyl, sulphinyl or sulphonyl moieties.
- 55 10. A method as claimed in any of Claims 1 to 6, wherein the composition comprises a resole resin, a novolak resin, a latent Bronsted acid and an infra-red absorbing compound.
11. A method as claimed in any of Claims 1 to 6, wherein the composition comprises a novolak resin, a radiation sensitive latent acid generating compound, a condensing agent for the novolak resin and an infra-red absorbing compound.

12. A method as claimed in any of Claims 1 to 6, wherein the composition comprises a phenolic resin and a photolysable onium salt.
- 5 13. A method as claimed in any preceding claim, wherein the composition includes a means for increasing the resistance of non-heated areas of the heat sensitive composition to dissolution in an aqueous developer (hereinafter the "developer resistor means"), wherein said developer resistor means comprises one or more compounds selected from the groups comprising:
  - (A) compounds which include a poly(alkylene oxide) unit;
  - 10 (B) siloxanes; and
  - (C) esters, ethers and amides of polyhydric alcohols.
14. A method as claimed in any of claims 1 to 3, wherein the composition comprises a phenolic resin and diazide moieties.
- 15 15. A positive working lithographic printing form precursor per se produced by a method as claimed in any preceding claim.
- 20 16. A method of producing a printing form, comprising an exposure step of effecting heating of selected areas of the composition of a precursor as claimed in Claim 15, such as to render such areas developer soluble, followed by development in an aqueous developer to remove said selected areas.
17. A lithographic printing form produced by a method as claimed in Claim 16.

#### Patentansprüche

1. Verfahren zur Herstellung eines Druckformvorläufers, welcher eine Beschichtung auf einem Träger umfasst, wobei die Beschichtung eine positiv arbeitende Zusammensetzung umfasst, welche ein Phenolharz umfasst, wobei das Verfahren zur Herstellung das Aufbringen der Zusammensetzung in einem Lösungsmittel auf den Träger, Trocknen der Zusammensetzung und die anschließende Wärmebehandlung des beschichteten Trägers umfasst, wobei die Wärmebehandlung über mindestens 4 Stunden durchgeführt wird.
- 30 2. Verfahren wie in Anspruch 1 beansprucht, wobei die Wärmebehandlung bei einer Temperatur im Bereich 40 bis 90 °C durchgeführt wird.
- 35 3. Verfahren wie in einem vorhergehenden Anspruch beansprucht, wobei das Trocknen der Zusammensetzung dadurch ausgeführt wird, dass der die Zusammensetzung in einem Lösungsmittel tragende Träger einer Temperatur ausgesetzt wird, welche die Temperatur, die zur Wärmebehandlung gewählt wurde, übersteigt und über eine Zeitdauer weniger als die, welche für die Wärmebehandlung gewählt wurde.
- 40 4. Verfahren wie in einem vorhergehenden Anspruch beansprucht, wobei die Zusammensetzung so geartet ist, dass ihre Löslichkeit in einem Entwickler durch einfallende UV-Strahlung nicht erhöht wird.
- 45 5. Verfahren wie in einem vorhergehenden Anspruch beansprucht, wobei die Zusammensetzung so geartet ist, dass sie mustergemäß direkter Wärme oder geladener Teilchenstrahlung oder elektromagnetischer Strahlung, welche jeweils durch die Beschichtung in Wärme umgewandelt wird, ausgesetzt werden kann.
- 50 6. Verfahren wie in Anspruch 5 beansprucht, wobei die Zusammensetzung so geartet ist, dass sie mustergemäß elektromagnetischer Strahlung einer Wellenlänge vollkommen oder überwiegend im Bereich 450 bis 1400 nm ausgesetzt werden kann, wobei die Beschichtung eine strahlungsabsorbierende Verbindung einschließt, welche die Strahlung absorbieren und in Wärme umwandeln kann.
- 55 7. Verfahren wie in einem vorhergehenden Anspruch beansprucht, wobei die Zusammensetzung ein in wässrigem Entwickler lösliches Phenolharz und eine Verbindung, welche die Löslichkeit des Phenolharzes im wässrigen Entwickler verringert, umfasst, wobei die Löslichkeit der Zusammensetzung im wässrigen Entwickler durch Erwärmen erhöht wird und die Löslichkeit der Zusammensetzung im wässrigen Entwickler durch einfallende UV-Strahlung nicht erhöht wird.

8. Verfahren wie in einem der Ansprüche 1 bis 6 beansprucht, wobei das Phenolharz mindestens eine der folgenden Definitionen erfüllt:

- es besitzt solche funktionellen Gruppen Q, dass das funktionalisierte Phenolharz die Eigenschaft hat, im Entwickler vor der Bereitstellung von Strahlung unlöslich und danach löslich zu sein, wobei die funktionellen Gruppen Q keinen Naphthochinondiazidrest oder Benzochinondiazidrest umfassen;
- es besitzt solche funktionellen Gruppen Q, dass das funktionalisierte Phenolharz die Eigenschaft hat, im Entwickler vor der Bereitstellung von Strahlung unlöslich und danach löslich zu sein, wobei die funktionellen Gruppen Q keinen Diazidrest enthalten;
- es besitzt solche funktionellen Gruppen Q, dass das funktionalisierte Phenolharz die Eigenschaft hat, im Entwickler vor der Bereitstellung von Strahlung unlöslich und danach löslich zu sein, wobei die funktionellen Gruppen beim Aussetzen gegenüber der Strahlung nicht chemisch zersetzt werden;
- es besitzt solche funktionellen Gruppen Q, dass das funktionalisierte Phenolharz die Eigenschaft hat, im Entwickler vor der Bereitstellung von Strahlung unlöslich und danach löslich zu sein, wobei die funktionellen Gruppen Q keine Säurereste oder säurebildenden Reste umfassen, jeweils durch labile Schutzgruppen geschützt, die beim Aussetzen gegenüber der Strahlung entfernt werden;
- es besitzt solche funktionellen Gruppe Q, dass das funktionalisierte Phenolharz die Eigenschaft hat, im Entwickler vor der Bereitstellung von Strahlung unlöslich und danach löslich zu sein, wobei die funktionellen Gruppen Q zusätzlich nicht hauptverantwortlich für die Absorption der Strahlung sind;
- es besitzt solche funktionellen Gruppen Q, dass das funktionalisierte Phenolharz die Eigenschaft hat, im Entwickler vor der Bereitstellung von Strahlung unlöslich und danach löslich zu sein, wobei es Wasserstoffbrückenbindungen zwischen den funktionellen Gruppen Q und anderen Resten des gleichen oder anderen/anderer Moleküls/e des polymeren Stoffs gibt.

9. Verfahren wie in Anspruch 8 beansprucht, wobei die funktionellen Gruppen Q ausgewählt werden aus Resten, die Amino-, Monoalkylamino-, Dialkylamino-, Amido-, Monoalkylamido-, Dialkylamido-, Chlor-, Fluor-, Carbonyl-, Sulfinyl- oder Sulfonyleinheiten umfassen.

10. Verfahren wie in einem der Ansprüche 1 bis 6 beansprucht, wobei die Zusammensetzung ein Resolharz, ein Novolakharz, eine latente Brönsted Säure und eine infrarot-absorbierende Verbindung umfasst.

11. Verfahren wie in einem der Ansprüche 1 bis 6 beansprucht, wobei die Zusammensetzung ein Novolakharz, eine strahlungsempfindliche, eine latente Säure bildende Verbindung, ein Kondensationsmittel für das Novolakharz und eine infrarot-absorbierende Verbindung umfasst.

12. Verfahren wie in einem der Ansprüche 1 bis 6 beansprucht, wobei die Zusammensetzung ein Phenolharz und ein photolysierbares Oniumsalz umfasst.

13. Verfahren wie einem vorhergehenden Anspruch beansprucht, wobei die Zusammensetzung ein Mittel zur Erhöhung der Lösungsbeständigkeit der nicht erwärmten Bereiche der wärmeempfindlichen Zusammensetzung in einem wässrigen Entwickler (nachfolgend "Entwicklerbeständigkeitsmittel") einschließt, wobei das Entwicklerbeständigkeitsmittel eine oder mehrere Verbindungen umfasst, ausgewählt aus:

- (A) Verbindungen, die eine Poly(alkylenoxid)einheit einschließen;
- (B) Siloxanen; und
- (C) Estern, Ethern und Amiden von mehrwertigen Alkoholen.

14. Verfahren wie in einem der Ansprüche 1 bis 3 beansprucht, wobei die Zusammensetzung ein Phenolharz und Diazideinheiten umfasst.

15. Positiv arbeitender, lithographischer Druckformvorläufer, als solcher hergestellt nach einem Verfahren wie in einem vorhergehenden Anspruch beansprucht.

16. Verfahren zur Herstellung einer Druckform, umfassend einen Bestrahlungsschritt zum Bewirken einer Erwärmung von ausgewählten Bereichen der Zusammensetzung eines Vorläufers wie in Anspruch 15 beansprucht, derartig dass die Bereiche entwicklerlöslich gemacht werden, gefolgt von Entwicklung in einem wässrigen Entwickler zur Entfernung der ausgewählten Bereiche.

17. Lithographische Druckform, hergestellt nach einem Verfahren wie in Anspruch 16 beansprucht.

## Revendications

1. Procédé de fabrication d'un précurseur de forme d'impression qui comprend un revêtement sur un substrat, le revêtement comprenant une composition fonctionnant de manière positive qui comprend une résine phénolique, dans lequel le procédé de fabrication comprend l'application de la composition dans un solvant sur le substrat, le séchage de la composition, et le traitement à la chaleur postérieur du substrat enduit, et dans lequel le traitement à la chaleur est effectué pendant au moins 4 heures.
2. Procédé selon la revendication 1, dans lequel le traitement à la chaleur est effectué à une température allant de 40 à 90°C.
3. Procédé selon l'une quelconque des revendications précédentes, dans lequel le séchage de la composition est effectué en soumettant le substrat portant la composition dans un solvant à une température dépassant la température sélectionnée pour le traitement à la chaleur, et durant une période de temps inférieure à celle sélectionnée pour le traitement à la chaleur.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la composition est telle que sa solubilité dans un révélateur n'est pas augmentée par un rayonnement UV incident.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite composition est telle qu'elle peut être exposée en modèle par chaleur directe, ou par un rayonnement à particule chargée ou par un rayonnement électromagnétique, étant dans chaque cas converti en chaleur par le revêtement.
6. Procédé selon la revendication 5, dans lequel la composition est telle qu'elle peut être exposée en modèle par un rayonnement électromagnétique d'une longueur d'onde entièrement ou de manière prédominante dans le champ de 450 à 1400 nm, dans lequel le revêtement comprend un composé absorbeur de rayonnement capable d'absorber ledit rayonnement et de le convertir en chaleur.
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel la composition comprend une résine phénolique soluble dans un révélateur aqueux et un composé qui réduit la solubilité de la résine phénolique dans un révélateur aqueux, dans lequel la solubilité dans un révélateur aqueux de la composition est augmentée en étant chauffée et la solubilité dans un révélateur aqueux de la composition n'est pas augmentée par un rayonnement UV incident.
8. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la résine phénolique rencontre au moins une des définitions suivantes :
  - a en son dessus des groupes fonctionnels Q, de telle sorte que la résine phénolique fonctionnalisée a la propriété d'être insoluble dans le révélateur antérieurement à l'émission de rayonnement et soluble dans le révélateur par la suite, dans laquelle les groupes fonctionnels Q ne comprennent pas un groupe de diazide de naphtoquinone ou diazide de benzoquinone ;
  - a en son dessus des groupes fonctionnels Q, de telle sorte que la résine phénolique fonctionnalisée a la propriété d'être insoluble dans le révélateur antérieurement à l'émission de rayonnement et soluble dans le révélateur par la suite, dans laquelle les groupes fonctionnels Q ne comprennent pas un groupe de diazides ;
  - a en son dessus des groupes fonctionnels Q, de telle sorte que la résine phénolique fonctionnalisée a la propriété d'être insoluble dans le révélateur antérieurement à l'émission de rayonnement et soluble dans le révélateur par la suite, dans laquelle les groupes fonctionnels ne se décomposent pas chimiquement à l'exposition dudit rayonnement ;
  - a en son dessus des groupes fonctionnels Q, de telle sorte que la résine phénolique fonctionnalisée a la propriété d'être insoluble dans le révélateur antérieurement à l'émission de rayonnement et soluble dans le révélateur par la suite, dans laquelle les groupes fonctionnels Q ne comprennent pas des groupes d'acides ou des groupes générateurs d'acide, protégés dans chaque cas par des groupes protecteurs labiles retirés à l'exposition dudit rayonnement ;
  - a en son dessus des groupes fonctionnels Q, de telle sorte que la résine phénolique fonctionnalisée a la propriété d'être insoluble dans le révélateur antérieurement à l'émission de rayonnement et soluble dans le

révélateur par la suite, dans laquelle les groupes fonctionnels Q ne sont pas responsables de manière additionnelle et primaire de l'absorption dudit rayonnement ;

- a en son dessus des groupes fonctionnels Q, de telle sorte que la résine phénolique fonctionnalisée a la propriété d'être insoluble dans le révélateur antérieurement à l'émission de rayonnement et soluble dans le révélateur par la suite, dans laquelle il y a un collage à l'hydrogène entre lesdits groupes fonctionnels Q et les autres groupes de la même molécule ou d'autre molécule(s) de la substance polymérique.

9. Procédé selon les revendications 8, dans lequel les groupes fonctionnels Q sont sélectionnés à partir de groupes comprenant des fractions aminées, monoalkylaminées, dialkylaminées, amidées, monoalkylamidées, dialkylaminées, chlorées, fluorées, carbonyles, sulphinyles ou sulfoniques.

10. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la composition comprend une résine résolique, une résine de novolaque, un acide de Bronsted latent et un composé absorbeur d'infrarouge.

11. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la composition comprend une résine de novolaque, un composé générateur d'acide latent sensible au rayonnement, un agent condensateur pour la résine de novolaque et un composé absorbeur d'infrarouge.

12. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la composition comprend une résine phénolique et un sel d'onium photolysable.

13. Procédé selon l'une quelconque des revendications précédentes, dans lequel la composition comprend un moyen pour augmenter la résistance des zones non-chauffées de la composition sensible à la chaleur à la dissolution dans un révélateur aqueux (ci-après le « moyen de résistance de révélateur »), dans lequel ledit moyen de résistance de révélateur comprend un ou plusieurs composés sélectionnés à partir des groupes comprenant :

(A) des composés qui comprennent une unité de poly(oxyde d'alkylène) ;

(A) des Siloxanes ; et

(B) des esters, éthers et amides d'alcools polyhydriques.

14. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel la composition comprend une résine phénolique et des fractions de diazide.

15. Précurseur de formes d'impression lithographiques fonctionnant de manière positive de par sa nature produit par un procédé selon n'importe quelle revendication précédente.

16. Procédé de production d'une forme d'impression, comprenant une étape d'exposition du chauffage effectif de zones sélectionnées de la composition d'un précurseur selon la revendication 15, de façon à rendre de telles zones solubles dans le révélateur, suivi d'un développement dans un révélateur aqueux pour retirer lesdites zones sélectionnées.

17. Forme d'impression lithographique produite par un procédé selon la revendication 16.